Crystallization of Monohydrocalcite in Silica-rich Alkaline Solution at Different Temperatures

/ GAN ZHANG, JUAN MORALES, CRISTÓBAL VERDUGO-ESCAMILLA, JUAN MANUEL GARCÍA-RUIZ (*)

(1) Laboratorio de Estudios Cristalográficos. Instituto Andaluz de Ciencias de la Tierra (CSIC-UGR). Avda. de Las Palmeras, 4, 18100 Armilla, Granada (Spain)

INTRODUCTION

The so-called "biomorphs" are a fascinating and beautiful group of polycrystalline, self-assembled silica-alkaline carbonate composite materials, which are usually obtained by crystallization process of carbonates with the presence of silica in alkaline environments. They are characterized by the hierarchy of their structures in addition to complex and curved morphologies which resemble the morphologies of crystallization under the control of living organisms. The first work related to biomorphs was reported in the 1980s, in which barium carbonate was slowly crystallized in alkaline silica gel by counterdiffusion method and biomorphic barium carbonate with non-crystallographic twisted ribbon was formed (Garcia-Ruiz, 1985).

However, up to now, the formation of silica carbonate biomorphs is only well studied for witherite and strontianite ($BaCO_3$ and $SrCO_3$, respectively) which are both orthorhombic crystals. Unlike the isomorphic minerals of barium carbonate and strontium carbonate, the formation of silica calcium carbonate is more complicated, since calcium carbonate is a polymorphic compound which contains different crystalline phases and lattices and only aragonite is confirmed to be able to produce silica carbonate biomorphs until now (Voinescu et al., 2008; Bitarello et al.,2010). Related to the morphologies found in biominerals, which are mainly attributable to the effect of organic molecules (Park and Meldrum, 2002), the crystallization of silica-carbonate biomorphs is a pure inorganic process without the presence of any organic matter.

Compared to calcite and aragonite, the stable anhydrous crystalline calcium carbonate under ambient conditions, monohydrocalcite ($CaCO_3{\cdot}H_2O$) is metastable and barely found in nature. This mineral was first reported in 1930 and its formation is normally related to the presence of magnesium in the crystallization media magnesium (Neumann and Epple, 2007), or during the dehydration of ikaite. However, previous studies have reported that monohydrocalcite with a hemispherical multi-layered structure could be steadily formed in $CaCO_3$ pure silica-rich alkaline solution without the presence of magnesium (Zhang et al., 2013), and the experimental conditions are similar to the environment where silica-carbonate biomorphs are formed, although the concentrations of reactant (carbonate anion and calcium cation) are more restrictive.

Here, we present the morphological study of the silica-calcium monohydrocalcite biomorphs obtained at different temperatures.

EXPERIMENTAL METHODS

Monohydrocalcite crystals (MHC) were prepared by diffusion in silica gel in a lab made crystallization cell. The setup consisted in a glass cassette where the bottom corresponded to the silica gel doped with sodium carbonate (0.05 M) while the upper part was occupied by the calcium chloride (0.05 M). The silica gel was prepared at room temperature and the final pH value was 10.5 ± 0.1. The carbonate contained gel precursor was injected into the cassette for gelling. The resulting carbonate contained silica gel was stored in a thermostatic oven to control the temperature. The injection of calcium chloride was considered the time zero of the crystallization time scale, and the crystallization process normally took 2 or 3 weeks. The experimental temperatures in the oven were set at 45 and 60 °C, respectively. Morphological characterization was monitored by using a Nikon AZ100 optical microscope. X-ray diffraction (XRD) and Raman microspectroscopy techniques were used to determine the nature of the crystalline phases.

At different stages of crystallization, crystals were extracted from the cell and cleaned in water and ethanol. After dried, they were coated by carbon and examined by a field emission scanning electron microscope (FESEM) with an AURIGA (Carl Zeiss SMT) system, equipped with energy-dispersive X-ray spectroscopy (EDX).

RESULTS AND DISCUSSION

After two weeks crystallization, micron-sized crystals were obtained in both liquid zone and liquid-gel interface. Biomorphic phases obtained either at 45 and 60 °C were confirmed to be monohydrocalcite by XRD (Fig. 1).

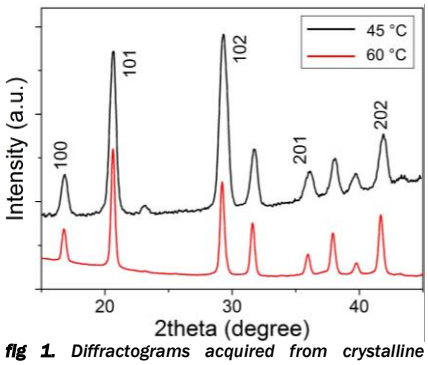

fig 1. *Diffractograms acquired from crystalline biomorphs obtained at 45 (black line) and 60 °C (red line).*

The results showed a strong morphological control of MHC by temperature. Compared to the hemispherical aggregates crystallized at room temperature by the same method (Zhang et al., 2013; 2015), several types of aggregates without the restriction of crystallographic symmetry were formed

palabras clave: Biomorfos, Monohidrocalcita, Cristalización auto-organizada

key words: Biomorphs, Monohydrocalcite, Self-assembled crystallization

* corresponding author: juanmanuel.garcia@csic.es

at higher temperatures. At 45°C, wood mushroom-like and twisted ribbon-like aggregates were observed (Fig. 2a). Similarly, coral-like aggregates were observed to form at 60 °C (Fig. 2b).

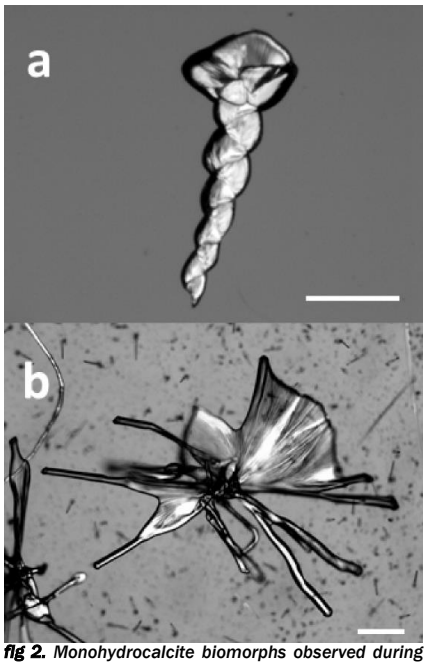

fig 2. *Monohydrocalcite biomorphs observed during crystallization experiment carried out at (a) 45 °C and (b) 60 °C. Image captured with a Nikon AZ100 microscope. (Scale bar: 200 µm)*

Textural analyses of the laminar and curvilinear sheets of wood mushroom-like MHC studied by FESEM confirmed that the growth was discontinuous during the crystallization process, and the aggregates exhibited a multilayered structure. The observation of the cross section of laminar sheets formed at 45 °C clearly showed a disruption between the sheets due to the discontinuous growth (Fig. 3). Similar behaviors of discontinuous growth were also observed at 60 °C.

FESEM images show that MHC was composed of nanocrystallites, co-arranged along the growth directions (marked by black arrows in Fig, 3), thus forming micron-scale rod-like subunits. The aggregates of the rod-like subunits were covered by an outer thin silica skin and therefore exhibited the multilayered structure (Fig. 3). Zhang et al. (2015) explained a growth mechanism as a coupled interaction between the reverse solubility of silica and carbonate versus local pH during crystallization of MHC at room temperature. This mechanism could also explain the growth behavior of MHC biomorph aggregates. The precipitation of calcium carbonate decreased the local pH leading to the increase of the supersaturation with respect to silica close to the growing front. This promoted the co-precipitation of silica as a skin and inhibited further growth of the calcium carbonate.

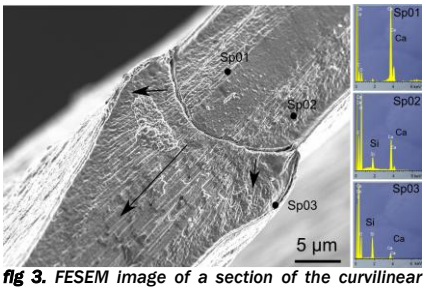

fig 3. *FESEM image of a section of the curvilinear sheet of MHC biomorph crystalized at 45°C. Some EDX spectra were collected at different positions (marked by black dots).*

EDX analyses carried out on the aggregates also indicated the changes of calcium and silica coupling between different parts of the sheet. The Ca peak was the only signal in the center part of the sheet (Fig. 3 Sp01), whereas Si peak could be observed as well as Ca peak in the part close to the outer thin skin (Fig. 3 Sp02). On the outer thin skin, Si was the major component (Fig. 3 Sp03). This corroborates the coupled interaction between carbonate and silica precipitation as well as the formation of a silica skin.

In situ Raman microspectroscopy was used to follow the crystallization process by time-lapse (12, 24 and 48 hours) measurements. All the spectra collected from the aggregates at 45 (Fig. 4) exhibited clear bands at 1067, 699 and 720 cm^{-1}, which are well documented as the symmetric stretching and the in-plane bending modes of carbonate group in MHC (Tlili et al., 2002).

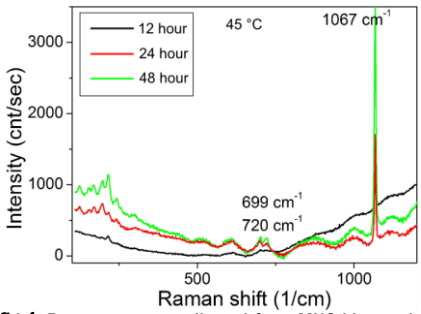

fig 4. *Raman spectra collected from MHC biomorph crystallized at 45°C and at different crystallization times: 12 hours (black), 24 hours (red) and 48 hours (green).*

These results confirmed that the crystallization of MHC was not the result of phase transition, but the result of nucleation.

In conclusion, biomorphs of MHC were crystallized in alkaline silica-rich conditions at different temperatures (45 and 60 °C). It is the first time that silica-carbonate biomorphs are reported to form without the aragonite-type lattice, demonstrating that the formation of biomorphs is not restricted to orthorhombic structure.

ACKNOWLEDGEMENTS

The research leading to these results has received funding from the European Research Council under the European Union's Seventh Framework Programme (FP7/2007-2013) ERC grant agreement nº 340863 / JAE-PRE program.

REFERENCES

Bittarello E., Roberto Massaro F., Aquilano D. (2010): The epitaxial role of silica groups in promoting the formation of silica/carbonate biomorphs: A first hypothesis. J. Cryst. Growth ***312****, 402-412.*

García-Ruiz, J. M. (1985): On the formation of induced morphology crystal aggregates. J. Cryst. Growth ***73****, 251-262.*

Neumann M. and Epple M. (2007): Monohydrocalcite and its relationship to hydrated amorphous calcium carbonate in biominerals. Eur. J. Inorg. Chem. 1953-1957.

Park R. J. & Meldrum F. C. (2002): Synthesis of Single Crystals of Calcite with Complex Morphologies. Adv. Mater. 14, 1167-1169.

Tlili M. M., Amor M. B., Gabrielli C., Joiret S., Maurin G., Rousseau P. (2002): Characterization of $CaCO_3$ hydrates by micro-Raman spectroscopy. J. Raman Spectrosc. ***33****, 10-16).*

Voinescu A. E., Kellermeier M., Bartel B., Carnerup A. M., Larsson A.-K., Touraud D., Kunz W., Kienle L., Pfitzner A., Hyde S. T. (2008): Inorganic self-organized silica aragonite biomorphic composites. Cryst. Growth Des. ***8****, 1515-1521.*

Zhang G., Delgado-López J. M., Choquesillo-Lazarte D., García-Ruiz J. M. (2013): Crystallization of monohydrocalcite in a silica-rich alkaline solution. Cryst. Eng. Comm, 6526-6532.

—, —, —, — (2015): Growth Behavior of Monohydrocalcite ($CaCO_3$·H_2O) in silica-rich alkaline solution. Cryst. Growth Des. ***15****, 564-572.*